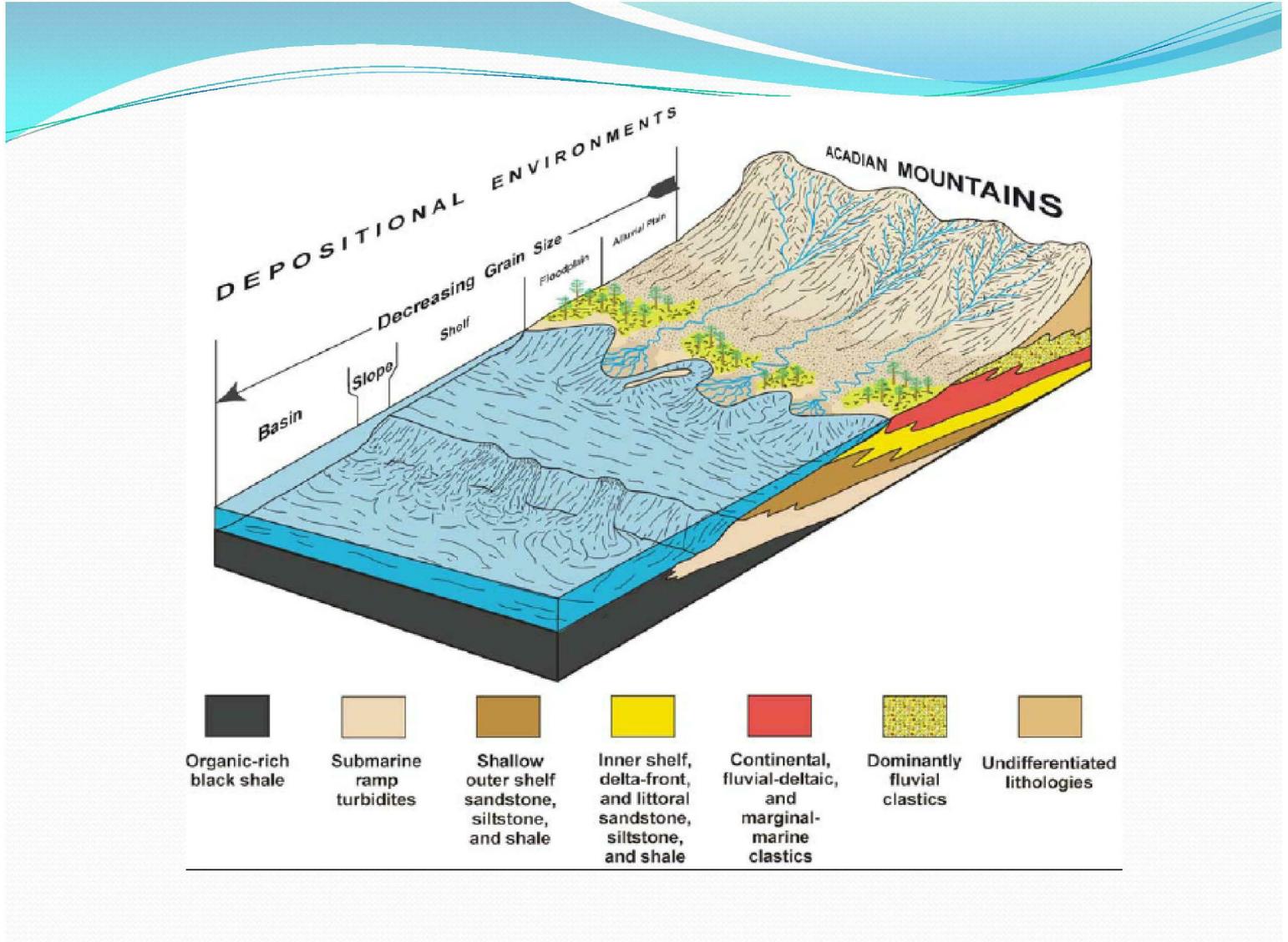


Isotech - Stable Isotope Analysis

Determining the origin of methane

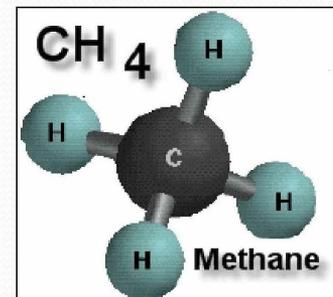
Environment of Deposition Middle Devonian (385 MA)





Methane is the principal hydrocarbon detected in all stray natural gas migration incidents

- Exposure limit (gas phase): TLV-TWA: 1,000 ppm (ACGIH, 10/2009)
- Methane (CH₄) is the simplest paraffin hydrocarbon gas
- Methane is generated by microbial & thermogenic processes
- Flammable, colorless, odorless.
- Specific gravity: 0.555 (NTP) air = 1
- Explosive range: 5-15% in ambient air
- Solubility in water: 26-32 mg/l (1 atm.)
- Non toxic, no ingestion hazard
- Simple asphyxiant, explosion hazard



Methane can migrate as free gas or dissolved in the groundwater



Isotopic Balance

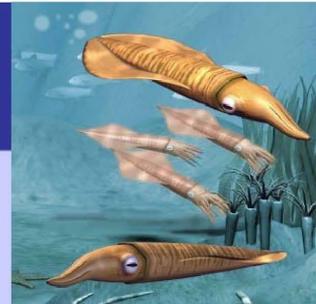
- Geologists trace the source of the carbon in hydrocarbons through analysis of its isotopic balance.
- Natural carbon is nearly all isotope 12, with 1.11 percent being isotope 13.
- Organic material contains less C-13, because bacteria /photosynthesis preferentially selects C-12 over C-13.
- Oil and natural gas typically show a C-12 to C-13 ratio similar to that of the biological materials from which they are to have originated.

Sh

- Increase in temperature ratio



Delta notation



Temperature (°C)

0

75

4)

0

225

$$\delta^{13}\text{C} = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}}$$

Where $R = {}^{13}\text{C}/{}^{12}\text{C}$,
 $R_{\text{reference}} = \text{VPDB (Vienna Pee Dee Belemnite)}$

- The $\delta^{13}\text{C}$ in
- Also

$$\delta^{13}\text{C} = \delta({}^{13}\text{C}) = \delta({}^{13}\text{C}/{}^{12}\text{C}) = \frac{n_{\text{X}}({}^{13}\text{C})/n_{\text{X}}({}^{12}\text{C}) - n_{\text{ref}}({}^{13}\text{C})/n_{\text{ref}}({}^{12}\text{C})}{n_{\text{ref}}({}^{13}\text{C})/n_{\text{ref}}({}^{12}\text{C})}$$

- Uni pair (e.g

Graphite

Isotope Geochemistry

- Molecular: Methane/Ethane
- Isotopic: Carbon and Hydrogen isotopes ($\delta^{13}\text{C}-\text{CH}_4$, $\delta^2\text{H}-\text{CH}_4$, $\delta^{13}\text{C}-\text{C}_2\text{H}_6$)
- Noble Gases

Easily Distinguishes:

- Biogenic vs. Thermogenic
(e.g. Schoell, 1983; Coleman et al, 1991; Baldassare and Laughrey, 1998)
- Distinguishing different thermogenic gases
(e.g. Schoell et al, 1983; Jenden et al, 1993; Revesz et al, 2010; Tilley et al, 2010)
- What's best for distinguishing thermally mature gases?





ANALYSIS REPORT

Lab #: 235488 Job #: 17407
 Sample Name/Number: HW02z
 Company: TechLaw, Inc.
 Date Sampled: 1/25/2012
 Container: Dissolved Gas Bottle
 Field/Site Name: A3TA
 Location:
 Formation/Depth:
 Sampling Point:
 Date Received: 2/03/2012 Date Reported: 2/20/2012

% carbon 13

% deuterium

% oxygen 18

% argon

% nitrogen

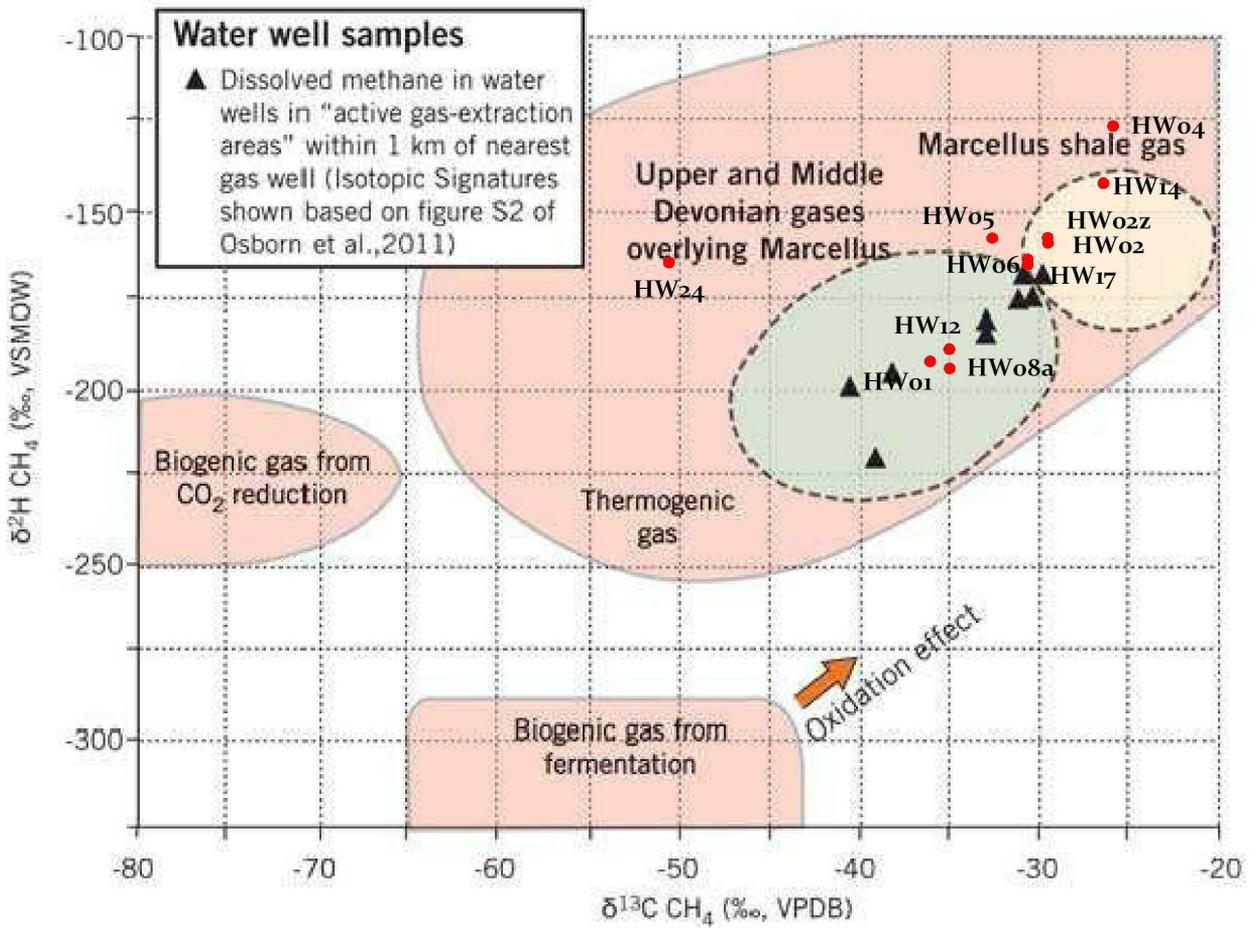
Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	δD ‰	$\delta^{18}\text{O}$ ‰
Carbon Monoxide -----	nd			
Hydrogen Sulfide -----	na			
Helium -----	0.0112			
Hydrogen -----	nd			
Argon -----	0.628			
Oxygen -----	0.80			
Nitrogen -----	40.72			
Carbon Dioxide -----	0.094			
Methane -----	57.06	-29.30	-160.6	
Ethane -----	0.687			
Ethylene -----	nd			
Propane -----	nd			
Propylene -----	0.0001			
Iso-butane -----	nd			
N-butane -----	nd			
Iso-pentane -----	nd			
N-pentane -----	nd			
Hexanes + -----	nd			
Water -----			-64.6	-9.66

-29

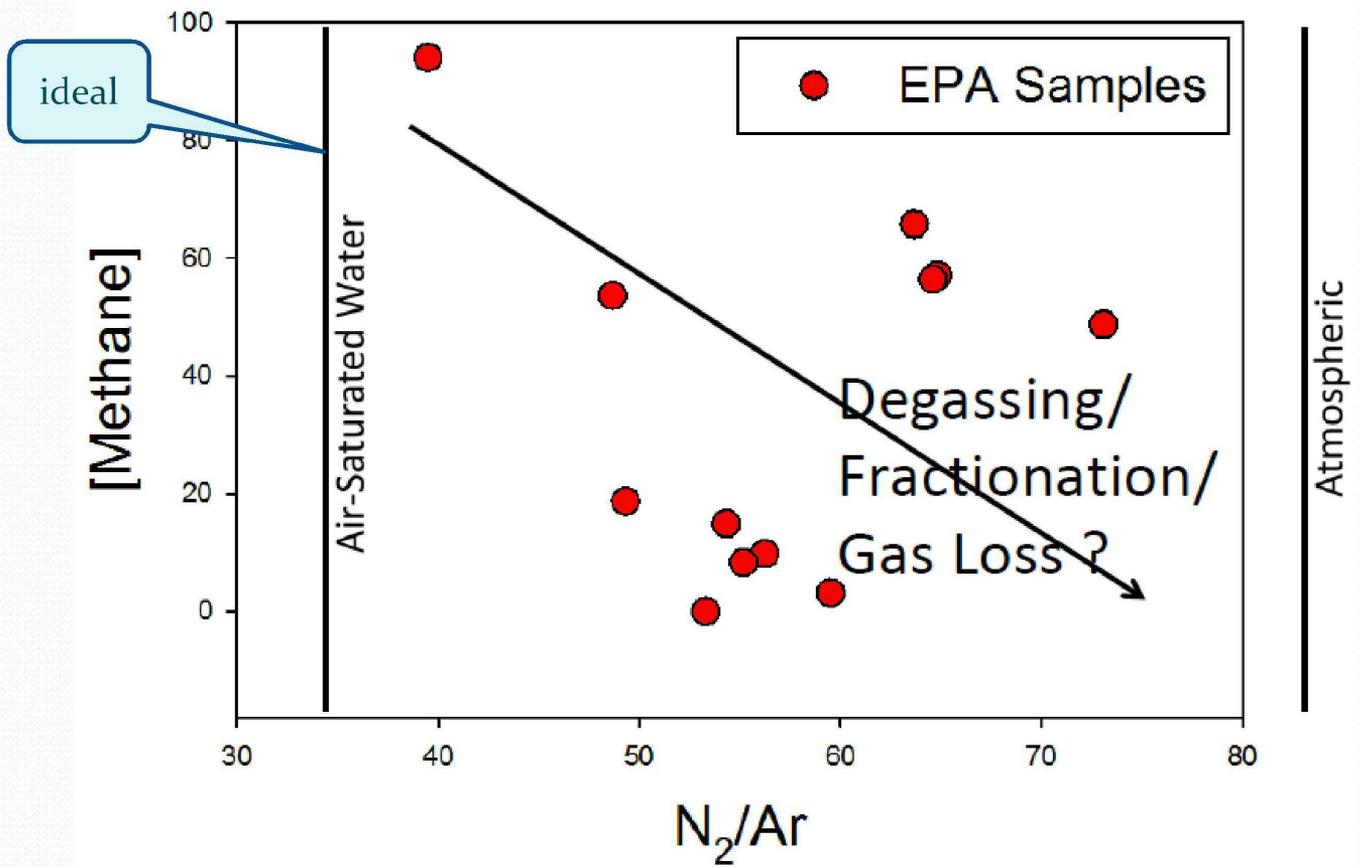
-160

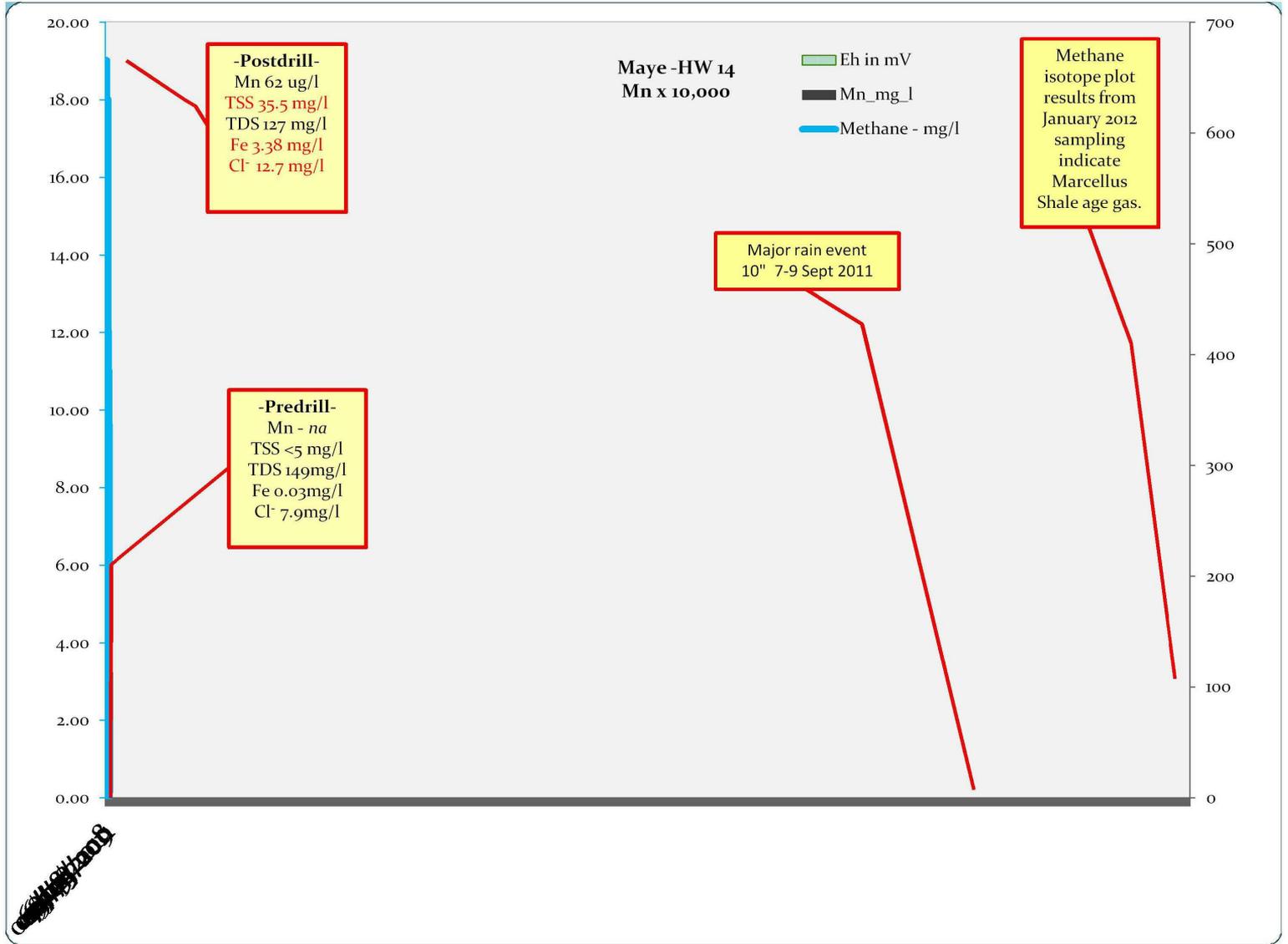
Total BTU/cu.ft. dry @ 60deg F & 14.7psia, calculated: 590

Specific gravity, calculated: 0.736



Sample Quality - degassing?





<u>Costello</u>	<u>1V</u>	<u>2V</u>
Spud Date:	7/26/08	8/19/08
Comp Date	9/12/08	11/11/08
Stim Date	9/30 /09	1/10/09

HW-2 Kemble

